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Storage Battery Engineering

BY ROBERT E. MUELLER, CH. E. '20

Because the passage of an electric current through a conductor often is compared with the flow of water through a pipe for purpose of analogy it has become a popular misconception in the minds of many people that the storage of electricity when charging a storage battery is very much the same as filling a bucket of water. This, however, is a misconception prevailing more among those who are uninformed rather than among engineers whose duties it may sometimes be to correct this erroneous conception so that the action and uses of such batteries may be better understood.

PRINCIPLE

In principle there is no essential difference between the action within an ordinary dry cell and the action within the cell of any storage battery upon discharging it, no matter whether the storage battery be of the lead-sulphuric acid or Edison alkali type. In each case we have a positive and negative electrode composed of two entirely different substances immersed in some kind of an electrolyte.

When such electrodes are connected through some external circuit—as a copper wire—chemical action takes place between the electrolyte and the electrodes to form new substances.

The usual products of electrolysis of dilute acid solutions are hydrogen and oxygen. The former appears at the cathode (—) while the latter appears at the anode (+); both appear as free gases unless the electrodes are of such chemical composition or nature as to combine with them. Twice as much hydrogen as oxygen is formed by volume. The heat energy when chemicals combine may manifest itself in the form of electrical energy. Due to the fact that there exists a difference of potential between two dissimilar substances, as sponge lead on the one side and lead peroxide on the other, we are provided with a useful electromotive force to carry the electrical energy from the chemical action within the cell to some external source, as a motor, and there made to perform useful work.

HISTORY

In 1745 Musschenbroek made the first attempt to store electricity in a bottle. He succeeded in storing it for thirty or more seconds but his experimentation only lead to the principle upon which his invention of the Leyden jar is based.

Other workers along these lines were Volta and Humbolt, neither of whom discovered anything of practical value to be applied to the storage battery.

But in the year 1860 Mr. Plante, a French physicist, immersed two sheets of lead in a dilute sulphuric acid solution and sent a current through this cell in one direction until the oxygen evolved at the anode, oxydized this plate to lead peroxide,

while any oxides on the cathode were reduced by the nascent hydrogen to an allotropic form of lead, known as sponge lead. He then discharged his cell and again recharged it by passing the current through in the opposite direction to the first, thereby reducing the previously formed lead peroxide to sponge lead and oxidizing the other plate to lead peroxide. And so, by repeatedly charging and discharging—making one plate positive and then the other—Mr. Plante was able to obtain a thick layer of active material on each plate. These plates were then said to be formed and this method, together with modifications, is still used in the formation of Plante plates.

In 1878 Faure discovered electrolytically prepared sponge lead obtained from lead oxides and its use in practical manufacture. His battery was composed of elements prepared entirely from lead sulphate.

In 1881 he took out a patent covering a method for preparing the active material which was mechanically applied to the surface of the plates. This eliminated the great number of reversals necessary in the Plante process. The difficulty experienced was to keep the coatings of "paste" on the plates.

But in 1885 Mr. Brush of Cleveland, Ohio, obtained a patent through the United States courts and after long litigation for the application of lead oxides to a supporting metallic grid. It was decided that Brush's invention preceeded Faure's application for a patent.

MANUFACTURE

In the following the writer will describe the manufacture of lead-sulphuric acid batteries as carried out by the Willard Storage Battery Co., Cleveland, Ohio, merely because he had become acquainted with their methods while in charge of their chemical laboratory where raw materials are constantly analyzed before being used and where factory products are controlled by chemical analysis. Frequently it also fell to the writer's lot to conduct visitors through the plant and explain the operations to them.

It is understood, however, that other manufacturers of lead-acid batteries do not materially depart from the same operations and processes.

Three types of lead-sulphuric acid batteries are made by the above firm according to the uses which are to be made of them.

1. Automobile starting and lighting batteries.
2. Stationary plant batteries.
3. Train lighting batteries.

1. AUTOMOBILE STARTING AND LIGHTING BATTERIES

The Problem. The problem of the starting and lighting battery industry is to produce a storage battery which has the greatest capacity per unit weight of the battery. For this reason

these batteries are composed of pasted plates rather than of heavier Plante formed plates.

Parts. There are a number of important parts to a storage battery of this type listed as follows:

A. Positive and negative pasted and formed plates.

B. Suitable separators.

C. A container or jar.

D. An electrolyte of sulphuric acid, Sp. Gr. 1.300.

E. A wooden acid-proof box into which the separator cells may be assembled.

F. Binding posts, connectors, covers and minor accessories which are necessary in building up a good, substantial battery.

Moulding the Grids. Formation of a metallic grid which is to hold the active material of the plate is brought about by casting a molten alloy of antimony and lead into a steel mould built to give the desired shape, size and thickness of the grid. An alloy containing from 5 to 7% of antimony with the balance of pure lead has been found best suited for this purpose.

Two grids of the ordinary size are cast together in one operation and later cut in two after the plate has been formed. Fig. 1 gives an illustration of such a grid, the structure of which may be altered without affecting the physical property of the grid.

After removal from the mould the rough grid must be finished by trimming off the excess of material by means of a suitable trimming press. Such trimmings form "scrap" lead which is returned to the smelter and added to other scraps of lead and oxides of lead for refinement and recovery.

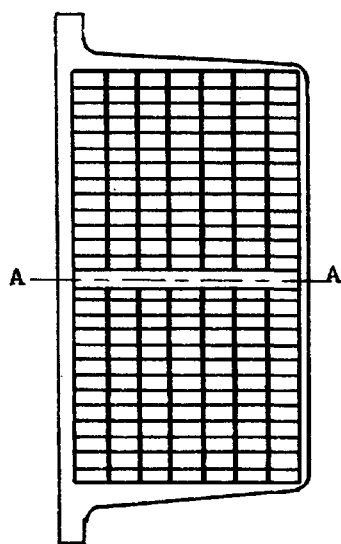


FIG. 1.

Pasting the Plate. For the positive plate a paste is made up of red lead, $2\text{PbO}-\text{PbO}_2$, mixed with a suitable binder and expander and then with sufficient dilute sulphuric acid to give the paste the proper consistency. The object here is to obtain the maximum porosity in the finished plate so that the greatest amount of active material may be available when chemical action proceeds.

This paste is then kneaded into the above grid by hand and the resulting plate dipped into dilute sulphuric acid solution to form a small amount of lead sulphate, PbSO_4 , which hardens the plate. These plates are then placed in a movable rack preparatory to passing through the dryer.

The negative plates are made up in the same manner, using litharge, PbO , instead of red lead. However, the latter could be used but it would take a great deal more electrical energy and time to reduce it way down to spongy lead, Pb ; but there would be no particular advantage in doing so and the process would be less economical.

The red lead and litharge thus used must be of the highest quality and purity, otherwise local action takes place within the cells and the efficiency of the battery would fall very rapidly. Copper and iron, for example, are among the most harmful foreign elements to look for by means of chemical analysis of the raw materials before they are used.

Drying. This operation is carried out by hauling the rack containing the pasted plates to the drying chamber which extends along the entire length of the building from one end to the other. This chamber is about 4 ft. broad, 6 ft. high and 75 ft. long, carrying an endless chain through its entire length. The chain moves very slowly along its own length and is hooked onto the bottom of the rack, which, then, automatically moves through the drying chamber while warmed air is passed through. The plates then emerge from the opposite end of the chamber in a dried condition.

Forming. Up to this point we have the positive plates pasted with red lead, $2\text{PbO}-\text{PbO}_2$, and the

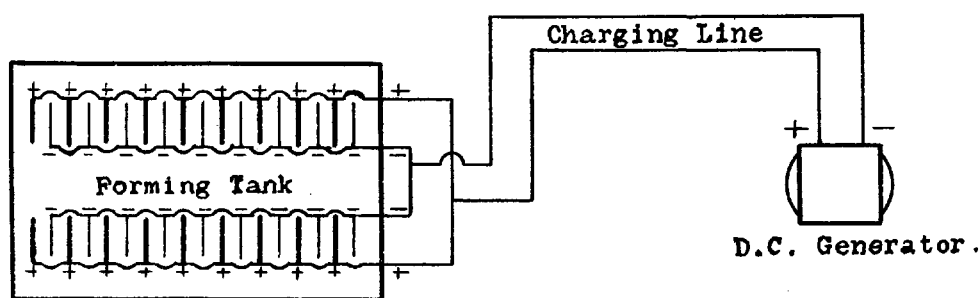


Figure 11.

negative with litharge, PbO . In this condition they are known as "green" plates.

Now, the object is to reduce the litharge to spongy lead and oxidize the red lead to lead peroxide. Part of the red lead is already in the form of lead peroxide—as seen from its chemical formula—and in the following process it is the balance of the red lead, i. e. the part represented by 2PbO , which is converted into the peroxide.

To accomplish this the above plates are subjected to a process known as "forming" in which a number of the plates are placed into a rectangular lead tank, provided with wooden racks having slots into which the plates may be inserted in an upright position. These tanks are called "forming tanks" and contain a sulphuric acid electrolyte. The positives and negatives are placed in an alternative order so that the lugs extend above the top of the tank. Like plates are then connected together temporarily by means of copper wire as shown in Fig. II, thus forming parallel circuits.

In this way all positive plates are connected to the positive side of the charging line while all negative plates are on the negative side. The forming current is a low voltage, high current rate, adjustable by means of a variable resistance in the circuit, the amount of current being determined by the size and number of plates. It must be a direct current. The electromotive force applied in forming must be somewhat greater than 2 volts per parallel circuit and it requires from 24 to 48 hours to completely convert the plates into the desired compounds after which the plates are said to be "formed."

This "forming" phenomena is of an electrochemical nature and can well be represented by the following reactions:

Negative: $2\text{PbO} \longrightarrow 2\text{Pb}$

Positive: $2\text{PbO} \cdot \text{PbO}_2 \longrightarrow 2\text{PbO}_2 \cdot \text{PbO}_2$

Summation $2\text{PbO} + \text{Pb}_2\text{O}_4 \longrightarrow 2\text{Pb} + 3\text{PbO}_2$

Upon being removed from the forming tanks the formed plates are at once taken to large, wooden vats where they are washed free from acid by running, cold water. They are then arranged carefully in large wooden racks where they are dried in air and stored until further use.

Inspection and Storage. At this stage of the process the careful manufacturer maintains a careful watch on the material turned out and it becomes the duty of experienced inspectors to scrap all physically defective plates, while the good material is passed on to the cutting department if two grids originally had been cast in one operation, or placed in storage if large, single plates are being handled.

Cutting. A suitable machine, having a holding die and a cutting die, issued to cut the doubly cast and formed plates into two similar parts, the cut being taken along the line A-A in Fig I. The resulting plates are placed in storage from which they are taken either for shipment to battery stations or for the next operation of assembling.

Assembling. The formed positive plates are placed in a rack with their lugs extending upward so that the lugs may be filed down to a uniform height. They are then connected together by burning a connector onto them, using an oxy-hydrogen flame. This process is called "lead-burning."

The connectors are made of pure, antimonious lead which is non-corrosible and having been previously cast in the moulding department. The number of plates to be assembled into such a group or "element" is predetermined by the capac-

ity of the battery which is under process of construction.

Similarly, a number of negative plates are arranged together to form negative elements. The number of plates in a negative group must always exceed the number of positive plates by one. The elements of opposite polarity are then telescoped together in the proper fashion and in this form are ready to receive the separator.

Two types of separators are now in general use, namely

(a) The Wood Separator.

(b) The Thread Rubber Insulator.

The former type, (a), is the older and has been used by storage battery producers for many years. This kind is made of the best grade of wood, such as bass wood, and a lot of them are chemically treated in order to eliminate the resinous material, thereby leaving a pure fibre having a very porous structure. The ordinary treatment consists in boiling the separators for a long time in a steel tank with a strong solution of caustic soda and then washing out the caustic by means of hot water.

The latter type, (b), is the newer type and is exclusively used by the Willard Storage Battery Co., since they have taken out a patent on its manufacture and use. The thread rubber insulator is composed of vulcanized rubber impregnated with many fine threads of cotton fibres to make it porous and to give it a certain degree of capillarity. It is claimed that the internal resistance of batteries equipped with the thread-rubber insulator has a lower resistance than those provided with the wood separators and, therefore, more efficient.

Among other differences between the wooden and rubber insulator stands the fact that eventually the former becomes charred by the action of the acid, thereby producing short circuits between the plates, while the vulcanized rubber insulator is acid proof and, therefore, much more durable.

The plates, as assembled, above, are placed upon a long bench in the center of which is a movable conveyor. As the elements are placed upon this table, moving slowly along, they are picked up by workers who insert either one or the other kind of separator between each positive and negative plate, depending on the grade of battery to be produced. The elements are then returned to the conveyor and later picked up and placed into a rubber jar of suitable size and fitted with the proper kind of rubber cover which is sealed in by means of a sealing compound. This sealing compound is made from an asphalt base, gilsonite, together with petroleum residum and is of an acid proof nature. We now have what is technically termed a battery unit, or cell.

The cells are taken from the movable conveyor and placed temporarily into large crates which hold 12 of the larger cells to 48 of the smaller. By means of copper wire like poles of all cells in a crate are connected together preparatory to an initial charge.

At the end of the conveyor a workman fills each cell with dilute sulphuric acid, Sp. Gr. 1.300, from a lead pipe and nozzle, the acid being stored in

a lead lined tank on the second floor of the building and being fed by gravity to its destination. The crate of cells is now removed from the conveyor and taken to the charging room.

Charging. The purpose of an initial charge is to get the active material into play. This is done by charging the cells at a low rate for a long time—about 24 to 48 hours—and carefully testing the specific gravity every hour to see how much acid has been absorbed by the oxides of lead. The proper gravity of the acid must be restored occasionally by the addition of "doping" acid, having a Sp. Gr. of 1.400.

Finishing. After charging the entire crates are taken to another assembling department where the finished battery is made. The individual cells are removed from the crate and various numbers of them placed properly into an acid proof battery box. To fasten these cells into the box, a melted sealing compound, mixed with shellac or varnish, is run into the bottom of the box before being used. Upon cooling the mass in the bottom solidifies and holds the cells firmly into their position.

The number of cells to be used depends entirely upon the capacity or type of battery desired. Each cell will produce a terminal voltage of 2. Therefore, if a 6-volt battery is wanted, three such cells are placed in the battery box and connected in series; i. e. the positive pole of the first cell being connected to the negative pole of the second cell, and the positive of the second being connected to the negative of the third. We then have one free positive and one free negative pole from which to draw our current. If a 12-volt battery is wanted, six such cells are connected together, and so on.

Connections of this kind are made by "straps" which are also moulded in the moulding department and consist of an alloy of antimonial lead.

The battery thus assembled is properly tested and cleaned and ready for use.

Shipping. A large shipping department is maintained where all batteries containing the electrolyte are packed in a manner which will prevent the crate from being upset. The so-called "Bone Dry Battery" is also shipped from this point, less care being necessary in packing because such batteries are shipped without the electrolyte, whereas the receiver must add the acid and give it the initial charge.

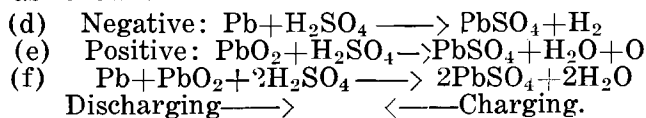
ACTION OF LEAD BATTERY

The electro-chemical conditions and action which takes place within a storage battery upon discharging and charging can be illustrated by the following steps (a), (b) and (c) and the chemical equations (d), (e) and (f).

		Beginning of Discharge.	
		End of Charge.	
(—)		H ₂ SO ₄	(+)
(a)	Pb	H ₂ O + SO ₂	PbO ₂
(b)	PbO	H ₂ O + SO ₂	PbO
(c)	PbO·SO ₂	H ₂ O	PbO·SO ₂
		End of Discharge.	
		Beginning of Charge.	

At (b) there is no more potentiality difference, hence the lack of current flow. Actually there exist no sharp boundaries between the various steps, but they take place gradually, finally ending up with lead sulphate in step (c) upon discharge.

The generally accepted theory of operation is as follows:



CARE IN HANDLING

The degree of care an ordinary automobile battery receives in the hands of amateur users is very small but the general abuse of a battery is very large. Many and various kinds of troubles arise daily due to lack of knowledge on the part of users as to what to do when a battery fails to function properly; but the best advice which can be given is to keep the battery away from garages and other places where a charging plant is in operation but where the proper handling of a storage battery is not understood.

Among the harmful things amateur battery men may do the following have been noted to be the surest:

1. **Overcharging.** They will overcharge a battery excessively to be sure that the customer secures his money's worth. The intention here is a good one, indeed, and no harm is contemplated. But this will cause overheating and, therefore, charring of the separators may take place. Consequently the plates within the cells will be short-circuited, the battery will fail to receive a charge and will not operate any longer. The customer becomes a prospect for a new battery and very likely will buy.

Overcharging also has the effect of evolving gases in excessive quantities which wash the active material from the positive plate. The oxides settle out and accumulate at the bottom of the cell and again short circuit the plates. Further attempt to charge such a battery will be useless.

2. **Doping the Electrolyte.** To bring up the gravity of the cell amateurs often resort to the addition of sulphuric acid which is a mistake more serious than it looks. This may strengthen the electrolyte to such an extent that charring of the separators is certain. If strong acid is used for this purpose the separators char immediately upon coming in contact with them. Hence, another method of easily ruining a battery.

3. **Further Doping.** It has been the pleasure of the writer to examine with interest numerous electrolytes and waters, which had been used by amateurs for storage battery work, as well as damaged plates as they were sent to the company's laboratory for inspection; possibly after bitter complaint by the user of the battery who earnestly declared not to have ruined the battery himself and expected a new one in return for his old one. Contamination of the electrolyte has caused the "death" of many a worthy battery as it becomes a martyr of its own fidelity.

For example, in one instance a well stoppered bottle was received from a service station manager in the far west whose customer had flushed his battery and then added freshly prepared, dilute sulphuric acid. The bottle contained a water white liquid, supposedly a sample of the water which he had diluted the acid. The substance seemed extraordinarily heavy.

The first test on any such liquid was to determine the Sp. Gr. by means of a hydrometer, expecting, of course, to be 1.000. But this hydrometer floated on the surface of the liquid like a cork. Further test, however, revealed the fact that this solution was one of a soluble lead salt.

Metallic mercury has even been found deposited on the negative plate, possibly added in the form of a solution as a "catalyzer."

Hence the conclusion, whenever any difficulty arises in the operation of a storage battery, it should be taken to an expert to remedy its faults, since he has studied, at least partly, the care and handling an ordinary secondary battery requires.

2. STATIONARY PLANT BATTERIES

The Problem. The problem of the stationary plant battery industry is to produce a storage battery for stationary purposes, such as farm lighting, etc.

The Parts. The parts used in this type of battery are essentially the same as in the starting and lighting battery industry with the following exceptions:

(a) The plates are of larger size, and, therefore, of greater capacity.

(b) The jar, instead of being made of hard rubber, is generally made of glass.

Operations. There are identical with the operations previously described except that elements, when assembled, are placed into the glass jars instead of rubber jars and the use of a conveyor is eliminated in assembling in order to reduce the possibility of breakage. Neither are conveyors here necessary because of the smaller number of such batteries produced.

3. TRAIN LIGHTING BATTERIES

The Problem. The problem of the storage battery industry for train lighting purposes is to produce a rechargeable storage battery to be used for supplying the current necessary for proper illumination of passenger pullmans and coaches.

The Parts. The essential parts of this type of battery are as follows:

- A. Positive and negative lead plates made by the Plante process.
- B. Perforated rubber separators.
- C. Rubber jars.
- D. Dilute Sulphuric acid electrolyte.
- E. Acid-proof wooden box.
- F. Binding posts, connectors, covers and straps together with other minor accessories.

OPERATIONS

Melting Lead. Pigs of pure lead are placed into a large iron kettle set into a gas heated furnace and the lead heated a little above its melting point so that it will flow well.

Pouring. The molten lead is then run into a steel mould, thereby casting a slab of pure lead $1\frac{1}{2}$ " thick by 20" square and allowed to cool.

Rolling. While still warm this slab is run back and forth between two steel rollers, each time reducing its thickness and elongating it until the required thickness, $\frac{3}{16}$ " to $\frac{1}{4}$ " is obtained, in this way obtaining long sheets of pure lead free from blow holes and dense.

Stamping. This long sheet of lead is then passed through a stamping machine which stamps out the plates in their desired shape. The stamping is done by means of a cutting die held firmly in the stamping machine.

Grooving. The purpose of this operation is to expose the maximum possible surface of the plate to the action of the forming acid in a later operation, and to provide a means of holding the formed lead peroxide or sponge lead onto the surface.

The stamped plates are, therefore, laid upon the table of the grooving machine, fastened down and grooved by means of a cutter fastened into a movable carriage. The surface of the plate is then "plowed" and the small ribs turned upright, perpendicularly to the surface of the plate, thereby forming small grooves very close together across the entire surface. Both sides of the plate are treated in this way before "forming."

Forming. This process of forming is the one previously mentioned in connection with Plante's experimentation and the plates so formed are known as Plante plates. They are very strong and durable as compared with the pasted type.

In this process temporary lugs are burned into the prepared plates which are placed into a lead lined tank having a dilute sulphuric acid electrolyte and a small amount of nitric acid or ammonium nitrate. They are placed between lead electrodes and an electric current sent through the system as in the forming of pasted plates, whereby the positive electrodes of PbO_2 are formed on the positive side and sponge lead is formed on the negative side of the line.

After these plates have been formed in this manner they, too, are disconnected from the charging line, washed with cold water to free them from acid and placed in a rack for drying and storage.

Assembling. The process of assembling is very much the same as the one previously mentioned under the manufacture of the starting and lighting battery, except that strong and durable, perforated hard rubber separators are inserted between each positive and negative plate.

The plates are much larger and consequently more difficult to handle. A larger acid proof box is necessary for the final assembly with porcelain insulators fastened to the bottom to insure against leakage of current.

A battery of long life and great capacity is thus made without the numerous troubles encountered in the pasted plate battery.